EXPERIMENTAL DETERMINATION OF LOW-PRESSURE SPECTRAL LINE INTENSITIES IN THE 5-мм O_2 BAND

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A device to measure the absorption coefficient in the 5-mm oxygen band at low pressures is described. Results of such measurements at resonant frequenciesin the 54–65 GHz range are presented. Experimental data are compared with the results from Rosenkranz's model theoretical calculations.

Studies of the absorbing properties of atmospheric gases are very important for remote monitoring of the state of the atmosphere. In particular, obtaining the dependence of the absorption coefficient γ of molecular oxygen on frequency ν, pressure P, and temperature T makes it possible to determine the vertical profile of atmospheric temperature from the measured parameters of upward microwave radiation.[1,2]

Currently many models are available for computing the O_2 absorption coefficient.[3–7] However, disagreement between their results amounts tens of per cent at certain values of ν, P, and T[8,9]. It is clearly stated in Ref. 10 that "the present-day state of knowledge on the oxygen absorption coefficient, as applied to the task of thermal sensing of the atmosphere, cannot be recognized as satisfactory". In such a situation the role of experimental studies of the dependence of γ on ν, P, T becomes extremely valuable.

To measure the O_2 absorption coefficient in the frequency range of 54–65 GHz at temperatures $T = 150–350$ K and pressures of $P = 0.1–10$ mm Hg we designed a special spectroscopic instrument. The intensity of absorption in the O_2 lines at such low pressures, corresponding to atmospheric heights of 30–60 km, is determined from a measurement of microwave radiation extinction in a waveguide cell.[11] The instrument was constructed following a microwave spectrometer scheme with molecular modulation and employed the Zeeman effect (the O_2 molecule possesses a dipole magnetic moment). A driving microwave generator 1 produces the initial signal, partially fed via a directional (coupler 3 into the calibrating channel which contains a phase inverter 4, attenuator 5, and a pin-modulator 7. The pin-diode modulator produces 100% amplitude modulation of the signal at the frequency of the reference generator 9, producing the magnetic field modulation. Having passed through all these elements, the signal directed by the directional couplers is mixed with the measurement channel signal 6. Then the signal passes though the measuring cell 10 and is fed into the microwave detector 11.

The measuring cell is a hermetically sealed waveguide, 1 m long, made from a silvered glass tube 12 mm in diameter. The modulating solenoid coils are wound directly upon the tube. Another coil is wound over the modulating solenoid to produce a constant magnetic field and compensate for the earth's magnetic field (when the cell is appropriately oriented along its lines of force).

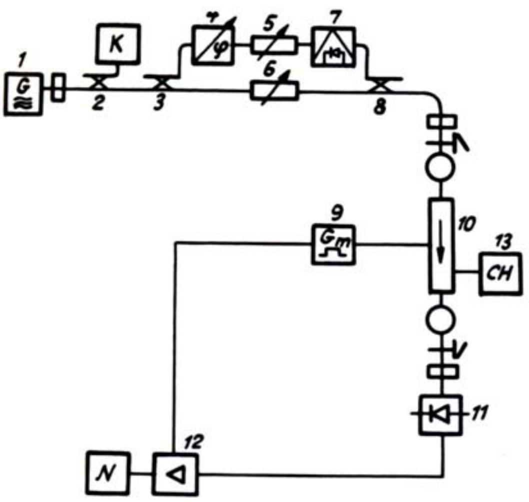

FIG. 1. Block diagram of the test set-up 1 – UHF generator; 2, 3, 8 – directional couplers; 4 – phase shifter; 5, 6 – attenuators; 7 – pin-modulator; 9 – magnetic field modulator; 10 – measuring cell; 11 – UHF detector; 12 – amplifier; 13 – gas mixture preparation unit.

The necessity of such compensation is explained by the fact that at pressures below 1 mm Hg the oxygen line width becomes comparable to the Zeeman splitting of each line in the earth's magnetic field. This splitting results in an additional measurement error in the absorption coefficient. The oxygen concentration and the mixture pressure in the cell are determined by the gas mixture preparation unit 13. The cell temperature is regulated by a thermostabilizing system.

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The absorption coefficient γ (cm^{-1}) is computed from the relationship

$$\gamma = \frac{2}{L} e^{-\alpha D}(1 - e^{-\alpha d}), \tag{1}$$

where L is the cell length, cm; D is the difference between extinctions in both channels, (dB); d is the modulation depth, (dB); $\alpha = \ln 10/20$.

According to (1) the relative error of the absorption coefficient measurement is equal to

$$\frac{\delta\gamma}{\gamma} = -\frac{\delta L}{L} - \alpha\cdot\delta D = \alpha\cdot\delta d/(e^{\alpha d} - 1), \tag{2}$$

where δL, δD, δd are the measurement errors for the values of L, D, d.

The errors δD, δd are caused by the effect of parasitic signals and reflections, by errors in the attenuator calibration, and by computation errors due to noises and various pickups.

Table I summarizes the estimated contributions from these errors for various values of γ, except for the error in cell length measurement, which can be ignored (0.1% for $L = 1$ m and $\delta L = 1$ mm).

TABLE I.

γ, cm^{-1}	D, dB	$\alpha\cdot\delta D$, %	$\frac{\alpha\cdot\delta d}{e^{\alpha l} - 1}$, %	$\frac{\delta\gamma}{\gamma}$, %
$2\cdot10^{-7}$	100	20	3	23
$2\cdot10^{-6}$	80	11	3	14
$2\cdot10^{-5}$	60	9	3	12

TABLE II.

The coefficient of absorption for molecular oxygen

Line number	Line frequency, MHz	$\bar{\gamma}$, cm^{-1}	δ, %
1^+	56264.78	$(4.71 \pm 0.25)\cdot10^{-6}$	- 10
3^+	58446.60	$(1.195 \pm 0.031)\cdot10^{-5}$	- 18
5^+	59590.98	$(1.70 \pm 0.25)\cdot10^{-5}$	- 22
7^+	60434.78	$(2.66 \pm 0.07)\cdot10^{-5}$	8.2
9^+	61150.57	$(2.18 \pm 0.02)\cdot10^{-5}$	-15
11^+	61800.17	$(2.39 \pm 0.04)\cdot10^{-5}$	2.9
13^+	62411.22	$(1.99 \pm 0.07)\cdot10^{-5}$	1.5
15^+	62998.00	$(1.025 \pm 0.012)\cdot10^{-5}$	-48
17^+	63568.52	$(8.48 \pm 0.32)\cdot10^{-6}$	-29
19^+	64127.78	$(7.66 \pm 0.05)\cdot10^{-6}$	2.6
21^+	64678.92	$(6.10 \pm 0.036)\cdot10^{-6}$	23
23^+	65224.08	$(2.69 \pm 0.037)\cdot10^{-6}$	-3.7

Thus, the relative error in measuring the absorption coefficient γ does not exceed 14% for $\gamma > 2\cdot10^{-6}\,cm^{-1}$. Such error estimates are preliminary, and should be refined from a statistical analysis of the empirical data presented below.

Table II lists measurement data on the O_2 absorption coefficient at resonance line frequencies for quantum numbers of 1^+–23^+, at a pressure of 1 mm Hg and temperature of 295 K. To assess random errors at each resonance frequency seven to nine measurements were taken for the lines of 1^+–17^+, and five to six measurements for the lines of 19^+, 21^+, and 23^+. It can be seen that errors lie within 1–5%, except for line 5^+, for which the error turned out to be 14%. Table III presents the measurement data on the absorption at resonance frequencies of the lines with quantum numbers 3^-–23^- for the same conditions. Here only four-five measurements were taken for each line, and the errors amounted to only 1–3%.

TABLE III.

The coefficient of absorption for molecular oxygen

Line number	Line frequency	$\bar{\gamma}$, cm^{-1}	δ, %
3^-	62486.25	$(1.54 \pm 0.04)\cdot10^{-5}$	-3.9
5^-	60396.057	$(1.67 \pm 0.05)\cdot10^{-5}$	-27
7^-	59164.204	$(1.83 \pm 0.02)\cdot10^{-5}$	-28
9^-	58323.874	$(1.6 \pm 0.01)\cdot10^{-5}$	-42
11^-	57612.481	$(1.825 \pm 0.017)\cdot10^{-5}$	-9.8
13^-	56968.180	$(1.77 \pm 0.03)\cdot10^{-5}$	7.9
15^-	56363.387	$(1.14 \pm 0.02)\cdot10^{-5}$	-7
17^-	55783.800	$(1.01 \pm 0.02)\cdot10^{-5}$	15.8
19^-	55221.365	$(0.7 \pm 0.02)\cdot10^{-5}$	21
21^-	54671.157	$(0.424 \pm 0.006)\cdot10^{-5}$	19
23^-	54129.999	$(2.66 \pm 0.06)\cdot10^{-6}$	29
25^-	53595.748	$(1.50 \pm 0.01)\cdot10^{-6}$	

To compare the obtained experimental data γ_e, with the theoretical values γ_c. Tables II and III also list the deviations $\delta = [(\gamma - \gamma_c)/\gamma_e\ I\cdot 100\%$.

The γ_c values were computed following Rosenkranz's model,[5] which, to a first approximation, accounts for line interference. According to this model the absorption coefficient is computed as

$$\gamma = CP^2\frac{\nu^2}{T^2}\left\{\sum_N \varepsilon_N f_{N^+}(\nu) + f_{N^+}(-\nu) + f_{N^-}(\nu) + f_{N^-}(-\nu)] + \frac{0.7\,\omega_b}{\nu^2 + P^2\omega_b^2}\right\}, \tag{3}$$

where $C = 0.18\cdot10^{-5}$ is the constant for calculating γ in cm^{-1}, (P is taken in mm Hg, and ν is in GHz). The summation is performed over the odd states from 1 to 39. The state occupancy N is calculated as

$$\varepsilon_N = \frac{2N + 1}{0.725N}\exp\left[-2.07\frac{N(N + 1)}{T}\right] \tag{4}$$

the line shape:

$$f_{N^{\pm}}(\nu) = \frac{w_N d^2_{N^{\pm}} + (\nu - \nu_{N^{\pm}})\cdot Y_{N^{\pm}}}{\left[\nu - \nu_{N^{\pm}}\right]^2 + (Pw_N)^2}; \tag{5}$$

the line amplitudes ν_{N^+} and ν_{N^-}

$$d_{N^+} = \left[\frac{N(2N+3)}{(N+1)(2N+1)}\right] \tag{6}$$

$$d_{N^-} = \left[\frac{(N+1)(2N-1)}{N(2N+1)}\right] \tag{7}$$

the nonresonance line width

$$w_b = 0.64\cdot 10^{-3}\left(\frac{300}{T}\right)^{0.89}, \tag{8}$$

the interference coupling coefficients between neighboring states due to molecular collisions

$$Y_{N^{\pm}} = d_{N^{\pm}}\left[\frac{2d_{N^{\pm+2}}\cdot w_{NU}}{\nu_{N^{\pm}} - \nu_{N^{\pm+2}}} - \frac{2d_{N^{\pm-2}}\cdot w_{ND}}{\nu_{N^{\pm}} - \nu_{N^{\pm-2}}} - \frac{w_b}{\nu_{N^{\pm}}} - \frac{w_b}{\nu_{N^{\pm}} + 60}\right]; \tag{9}$$

the resonance half-widths

$$w_N = 1.55\cdot 10^{-3}\left(\frac{300}{T}\right)^{0.85}, \tag{10}$$

Finally, collision broadening of the lines is computed in two steps from the relationships

$$w_{ND} = w_b - w_N - w_{NU} \tag{11}$$

$$w_{N-2,U} = w_{DN}\,\frac{\varepsilon_N}{\varepsilon_{N-2}}. \tag{12}$$

The absorption coefficient was computed according to a special program, employing the relationships (3)–(12).

Comparison of the empirical and computed values makes it possible to draw the following conclusions. The discrepancy δ does not exceed 4% for lines 11^+, 13^+, 19^+, 23^+, and remains below 14% for lines 1^+, 7^+, and 9^+. The experimental differ from the theoretical values by less than 14% for lines 3^-, 11^-, 13^-, 15^-. Note that the δ value for each line except line 13^+ is more than the random error (in the latter case δ = 1.5%, and the И* random li error is 3.5%). The analysis of data from the described instrument can help to select a model to compute an optimal absorption coefficient for specific tasks.

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